

Dendronized Poly(2-oxazoline) Displays within only Five Monomer Repeat Units Liquid Quasicrystal, A15 and σ Frank–Kasper PhasesMarian N. Holerca,[†] Dipankar Sahoo,^{†,‡} Benjamin E. Partridge,^{†,§} Mihai Peterca,^{†,§} Xiangbing Zeng,[§] Goran Ungar,^{§,||} and Virgil Percec^{*,†,||}[†]Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States[‡]Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396, United States[§]Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, United Kingdom^{||}State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

S Supporting Information

ABSTRACT: Liquid quasicrystals (LQC) have been discovered in self-assembling benzyl ether, biphenylmethyl ether, phenylpropyl ether, biphenylpropyl ether and some of their hybrid dendrons and subsequently in block copolymers, surfactants and other assemblies. These quasicrystalline arrays, which lack long-range translational periodicity, are approximated by two Frank–Kasper periodic arrays, $Pm\bar{3}n$ cubic (Frank–Kasper A15) and $P4_2/mnm$ tetragonal (Frank–Kasper σ), which have been discovered in complex soft matter in the same order and compounds. Poly(2-oxazoline)s dendronized with (3,4) $nG1$ minidendrons (where n denotes an alkyl chain, C_nH_{2n+1}) self-organize into the $Pm\bar{3}n$ cubic phase ($n = 14$ and 15) and, as reported recently, the $P4_2/mnm$ tetragonal phase ($n = 16$). However, no LQC of a poly(2-oxazoline) is yet known. Here we report the synthesis, structural and retrostructural analysis of a dendronized poly(2-oxazoline) with $n = 17$ which self-organizes not only into the LQC but also in the above two Frank–Kasper approximants. All three phases are observed from the same polymer within a very narrow range of degree of polymerization that corresponds to only five monomer repeat units ($5 \leq DP \leq 10$). The formation of the $Pm\bar{3}n$ cubic, $P4_2/mnm$ tetragonal and LQC phases from a single polymer chain within such a narrow range of DP raises the questions of how and why each of these phases is self-organized. This system may provide a model for theoretical investigations into the self-organization of soft matter into Frank–Kasper and related periodic and quasiperiodic arrays.

Frank–Kasper phases, elaborated in metals and their alloys in the 1950s,¹ were first discovered in complex soft matter² with self-assembling benzyl ether,³ biphenylmethyl ether,⁴ phenylpropyl ether⁵ and biphenylpropyl ether⁶ and with some of their hybrid⁷ dendrons and dendrimers.⁸ These supramolecular dendrimers facilitated discovery of both the $Pm\bar{3}n$ cubic (Frank–Kasper A15) phase^{2a–d} and the $P4_2/mnm$ tetragonal (Frank–Kasper σ) phase,^{2e} both of which are approximants for dodecagonal liquid quasicrystals (LQC)^{2f,9}

discovered for self-assembling dendrons a few years later.^{2f} Subsequently, these three periodic and quasiperiodic arrays,¹⁰ and additional Frank–Kasper phases including the C14 and C15 Laves phases,¹¹ have been transplanted to other types of soft matter^{12,13} including block copolymers,^{11b,14} lyotropic surfactants,¹⁵ lipids and glycolipids,¹⁶ colloidal nanocrystals,¹⁷ and molecules based on silsesquioxane cages.¹⁸ Frank–Kasper phases and quasicrystals generated from soft matter have been subjected to various theoretical investigations that have examined the energetic and entropic basis for their formation.^{9c,10,19}

Dendronized poly(2-oxazoline)s were one of the earliest scaffolds used for the discovery of periodic arrays,^{20,21} and have experienced a recent resurgence in interest due to potential applications as biomaterials.²² Poly(2-oxazoline)s with (3,4- $nG1$) benzyl ether dendrons (where n denotes an alkyl chain, C_nH_{2n+1}) with $n = 14$ or 15 self-organized into $Pm\bar{3}n$ cubic (Frank–Kasper A15) arrays,^{21b} while poly(2-oxazoline)s with (3,4,5-12G1) minidendrons facilitated discovery of the first body-centered cubic phase for supramolecular dendrimers.²³ The (3,4,5-12G1)-dendronized polymer also self-organized into a phase that could not be elucidated at that time and was later shown to be the $P4_2/mnm$ tetragonal phase.^{2e} Dendronized poly(2-oxazoline)s with $n = 16$ were recently shown to also generate the $P4_2/mnm$ tetragonal phase.²⁴ However, despite the observation of both $Pm\bar{3}n$ cubic and $P4_2/mnm$ tetragonal phases in dendronized poly(2-oxazoline)s, liquid quasicrystals, which $Pm\bar{3}n$ and $P4_2/mnm$ approximate,¹⁰ remained elusive. Progress in these fields prompted this Communication. In this report, a poly(2-oxazoline) dendronized with (3,4)-17G1-dendrons is reported to self-organize not only into $Pm\bar{3}n$ cubic and $P4_2/mnm$ tetragonal phases but also into a dodecagonal LQC. The self-assembly of poly[(3,4)-17G1Ox] into the LQC phase and two periodic approximants provides the whole range of Frank–Kasper phases known for self-assembling dendrons accessible from a single polymer chain within a range of only 5 monomer repeat units ($5 \leq DP \leq 10$).

The synthesis of the monomer (3,4)17G1-Ox and its living cationic ring-opening polymerization are shown in Scheme 1.

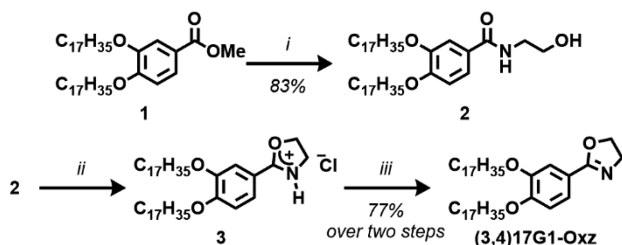
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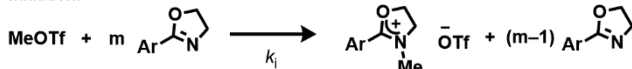


Scheme 1. Synthesis of (3,4)17G1-Oxz^a and Its Living Cationic Ring Opening Polymerization^b

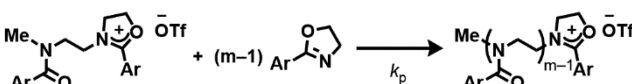
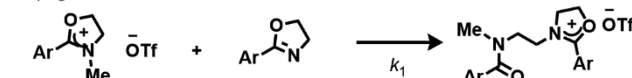
Synthesis of Monomer:



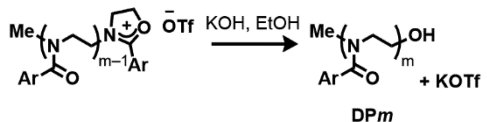
Initiation:



Propagation:



Termination:



^aReagents and conditions: (i) ethanolamine, 140 °C, 20 h; (ii) SOCl₂, CH₂Cl₂, 23 °C, 30 min; (iii) aq. NaHCO₃, 23 °C, 1 h. ^b*m* = 5, 10, 20, 40, 75, and 100. Polymerization temperature: 160 °C.

Alkylated ester **1**, prepared according to procedures routinely employed in our laboratory,²⁵ was reacted in bulk with excess ethanolamine at 140 °C for 20 h to give amide **2** in 83% yield after recrystallization from acetone. Treatment of **2** with SOCl₂ at 23 °C (15 min) to generate the corresponding oxazolinium chloride **3** *in situ*, followed by weak base deprotonation at 23 °C afforded dendronized 2-oxazoline (3,4)17G1-Oxz in 77% yield.^{21,24,26} Living cationic ring-opening polymerization in bulk at 160 °C using methyl triflate as initiator followed by end-capping with aq. KOH provided polymers with DP of 5, 10, 20, 40, 75, and 100, denoted DP*m*, where *m* is the number of monomer repeat units in the polymer chain.^{21,24}

Poly[(3,4)17G1-Oxz] with all DPs (DP*m*, 5 ≤ *m* ≤ 100) exhibit an undetermined crystalline phase, *k*, at low temperature, as indicated by a large endotherm observed by differential scanning calorimetry (DSC) upon heating (Figure 1) and confirmed by synchrotron X-ray diffraction (XRD, Figure 2). Upon further heating (Figures 1a and 2a), DP5 generates a liquid crystalline columnar hexagonal phase, Φ_h, and above 70 °C DP5 reorganizes into a *Pm* $\bar{3}$ *n* cubic (Cub) array. Subsequent cooling (Figure 2b) from the isotropic melt (*i*) does not reform the Cub but instead generates a *P*₄₂/*mnm* tetragonal (Tet) phase (Figure 2c), followed by Φ_h and *k*. The formation of both Cub and Tet from a single polymer with a single DP has not been observed before for poly(2-oxazoline)s.

All polymers with DP > 5 exhibit only a single phase between *k* and *i* observed both upon heating and cooling (Figure 1). For DP75 and DP100, this phase is a Φ_h array related to that observed for DP5 discs (Figure SF1) except it is assembled from

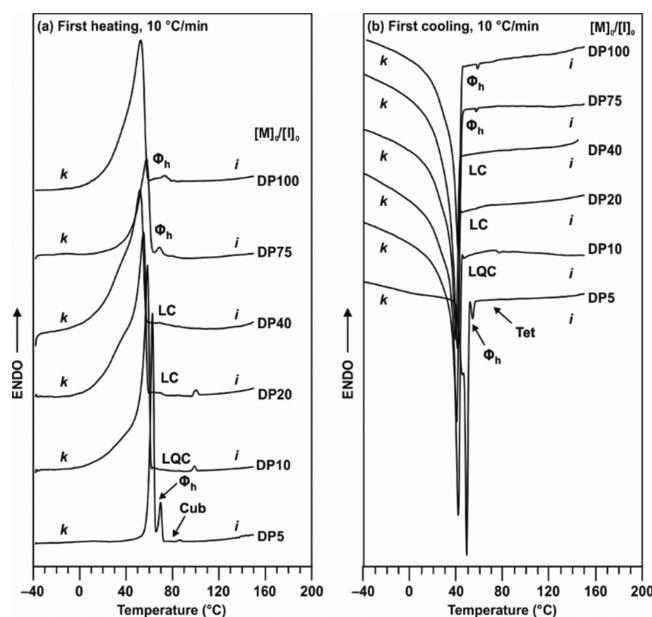


Figure 1. DSC traces of poly[(3,4)17G1-Oxz] recorded upon (a) first heating and (b) first cooling at a rate of 10 °C/min. Phases determined by XRD are indicated and defined in main text.

helical backbones.²⁴ DP20 and DP40 generate a liquid crystalline phase that could not yet be determined, denoted LC.

In contrast, DP10 generates a single phase between 56 and 99 °C that is neither Cub nor Tet. XRD data (Figure 2d) are consistent with a dodecagonal liquid quasicrystal (LQC).^{2f} The formation of a quasiperiodic array is unprecedented for poly(2-oxazoline)s. Poly[(3,4)17G1-Oxz] provides a single polymer chain that, within the DP range 5 ≤ *m* ≤ 10, self-organizes not only into the Cub and Tet phases but also into the LQC array for which Cub and Tet are approximants. Schematic depictions of Cub, Tet, and LQC are provided in Figure 2e. Full thermal and structural analysis parameters are provided in Table ST1 and Table 1, respectively. It is noteworthy that for DP5 and DP10, there is good agreement between *M*_{n,th} and *M*_{n,GPC}, while at higher DP values, *M*_{n,GPC} underestimates the *M*_{n,th}. This agrees with previous results on dendronized polymers from our laboratory.^{2c,g} The increased rigidity of the polymer backbone at high DPs changes the hydrodynamic volume of the polymer, increasing its elution time and underestimating *M*_n. This underestimation increases with increasing polymer molecular weight and can reach a factor of more than 10× (ref 2g, Table 3). The 2× to 3× observed for these poly(oxazoline)s is thus consistent with previous data.^{2c,g} At low DPs in spherical assemblies, chain conformation is random-coil and therefore is not underestimated by GPC.^{2c,g} Similar detailed studies for poly(oxazoline)s lie beyond the scope of this paper but will be reported with other poly(oxazoline)s in an independent publication.

The supramolecular spheres of the Cub and Tet phases generated by DP5 are very similar. Lattice parameters determined by XRD (Figure 2 and Table 1) indicate that the diameter of the supramolecular sphere, *D*_{sphere}, of DP5 is 54.2 Å in Cub and 55.4 Å in Tet. Retrostructural analysis (Table 1) suggests that the number of polymer chains per sphere, μ, is 15 in Cub and 16 in Tet. Because of the narrow polydispersity of poly[(3,4)17G1-Oxz]²¹ (Table ST1) and the difference in the volume of different spheres within a *Pm* $\bar{3}$ *n* or *P*₄₂/*mnm* unit cell,²⁷ these values for μ present an idealized approximation of

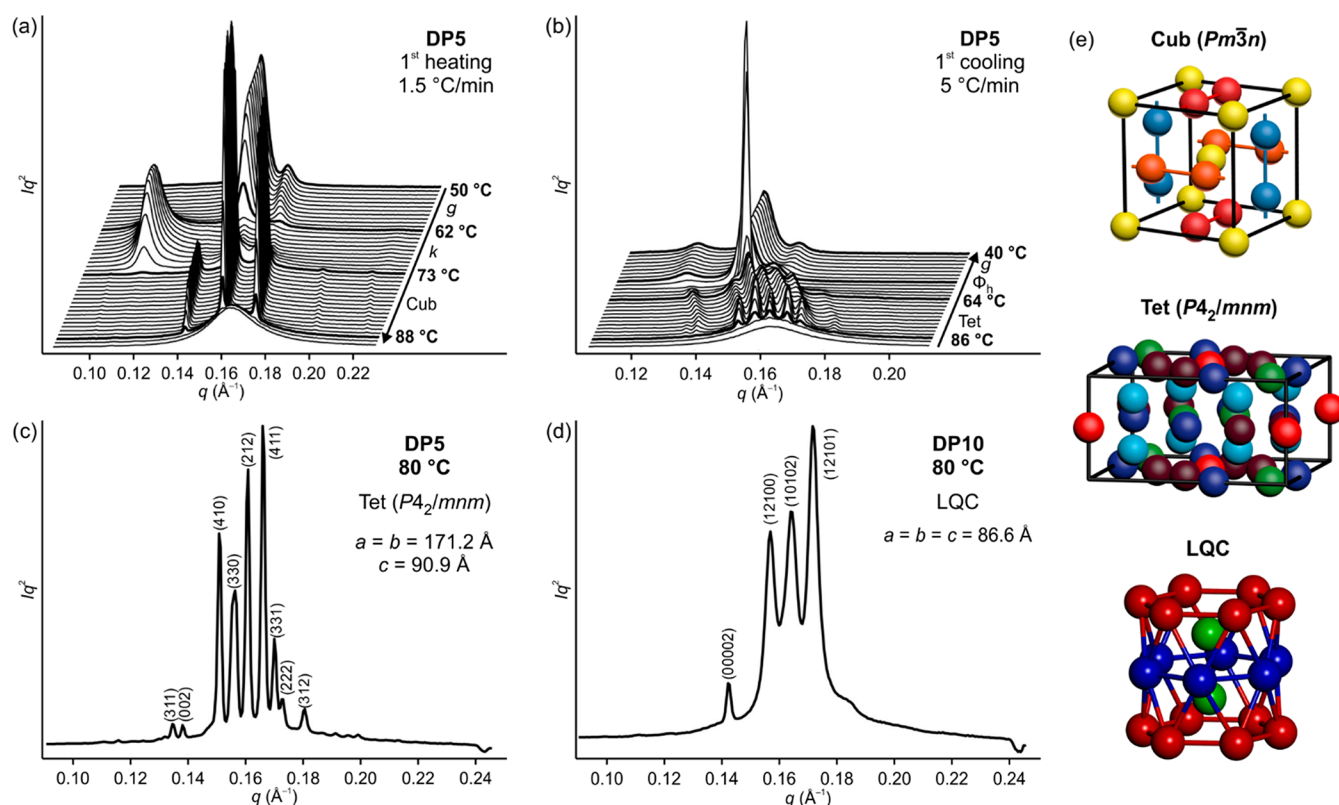


Figure 2. Powder XRD. (a) First heating of DP5 at 1.5 °C/min. (b) First cooling of DP5 at 5 °C/min. (c) **Tet** phase of DP5 at 80 °C. (d) **LQC** phase of DP10 at 80 °C. (e) Schematic depictions of **Cub**, **Tet**, and **LQC**.

Table 1. Structural and Retrostructural Analysis of DP5 and DP10

	T (°C)	Phase	a (=b), c (Å) ^{<i>a</i>}	d_{100} (Φ _h); d_{200} , d_{210} , d_{211} (Cub); d_{311} , d_{002} , d_{410} , d_{330} , d_{212} , d_{411} , d_{331} , d_{222} , d_{312} (Tet); d_{00002} , d_{12100} , d_{10102} , d_{12101} (LQC) (Å) ^{<i>b</i>}	D_{sphere} (Å)	M_{wt} (g/mol)	μ_{cell} ^{<i>c</i>}	μ ^{<i>d</i>}	μ^e
DP5	54 ^{<i>f</i>}	Φ _h	46.5, —	40.26 (40.26)	—	3,339	—	—	—
DP5	88 ^{<i>g</i>}	Cub	87.3, 87.3	43.63 (43.66), 39.05 (39.05), 35.66 (35.65)	54.2	3,339	121	15.1~15	76
DP5	80 ^{<i>f</i>}	Tet	171.2, 90.9	46.60 (46.51), 45.44 (45.44), 41.56 (41.52), 40.24 (40.35), 39.03 (39.08), 37.79 (37.76), 36.89 (36.88), 36.36 (36.34), 34.79 (34.80)	55.4	3,339	484	16.1~16	81
DP10	70 ^{<i>f</i>}	LQC	86.6, 86.6	44.10 (43.32), 40.04 (40.21), 38.26 (38.75), 36.56 (36.47)	59.1	6,714	59	9.9~10	99

^aCell parameters. ^bExperimental (calculated) *d*-spacings. ^cNumber of molecules in the unit cell. ^dNumber of molecules in the supramolecular sphere. ^eNumber of monodendritic units in the supramolecular sphere. ^fMeasured upon cooling. ^gMeasured upon heating. Details of calculations for structural and retrostructural analysis are provided in SI Section 5.

the number of DP5 chains in an average supramolecular sphere. Nevertheless, the supramolecular sphere of DP5 in the **Cub** and **Tet** phases is almost identical (Figure 3a–d).

Sixteen DP5 polymer chains, each adopting a conical conformation (Figure 3a–c), assemble into a supramolecular sphere (Figure 3d). This sphere contains 75–80 dendrons (determined by multiplying the number of dendrons per chain, *m*, by the number of chains per sphere, *μ*), substantially higher than the 60 dendrons that formed the supramolecular spheres of the **Cub** and **Tet** phases of poly[(3,4)16G1-Oxz].²⁴ Structural and retrostructural analysis of DP10 demonstrates that the **LQC** phase is generated from supramolecular spheres of diameter 59.1 Å containing approximately 10 polymer chains (Figure 3e–h). This corresponds to ~100 dendrons, substantially larger than the supramolecular spheres of poly[(3,4)16G1-Oxz]²⁴ or poly[(3,4)17G1-Oxz] (Figure 3a–d) that generate the **Cub** and **Tet** phases. The Φ_h phase of DP5 is constructed from disc-like polymer chains that stack into columnar arrays (Figure SF1).

The *Pm3n* cubic (**Cub**) phase is observed more often for self-assembling dendrons than either of the **Tet** or **LQC** phases. This is typically rationalized by considering the higher degree of deformation²⁸ accommodated within a *Pm3n* (**Cub**) unit cell (which must fill all space with only two distinct types of spheres, or more accurately, Wigner–Seitz cells)²⁷ compared to a *P4₂/mnm* (**Tet**) unit cell (in which there are five distinct types). The ability of spheres to undergo deformation, which reduces unfavorable repulsive interactions between neighboring spheres,^{2e,28} typically changes as a function of DP. However, for poly[(3,4)17G1-Oxz], both the **Cub** and **Tet** phases are generated by almost identical supramolecular spheres of DP5 (Figure 3d). Furthermore, the supramolecular sphere of DP10 (Figure 3h) might be assumed to have a similar deformability to the sphere of DP5 but assembles into an **LQC** phase rather than a **Cub** or **Tet** phase. Theoretical work has suggested that the presence of mobile surface entities and shape polydispersity may encourage formation of quasiperiodic arrays.^{19b} However, the presence of different surface mobilities or shape polydispersities

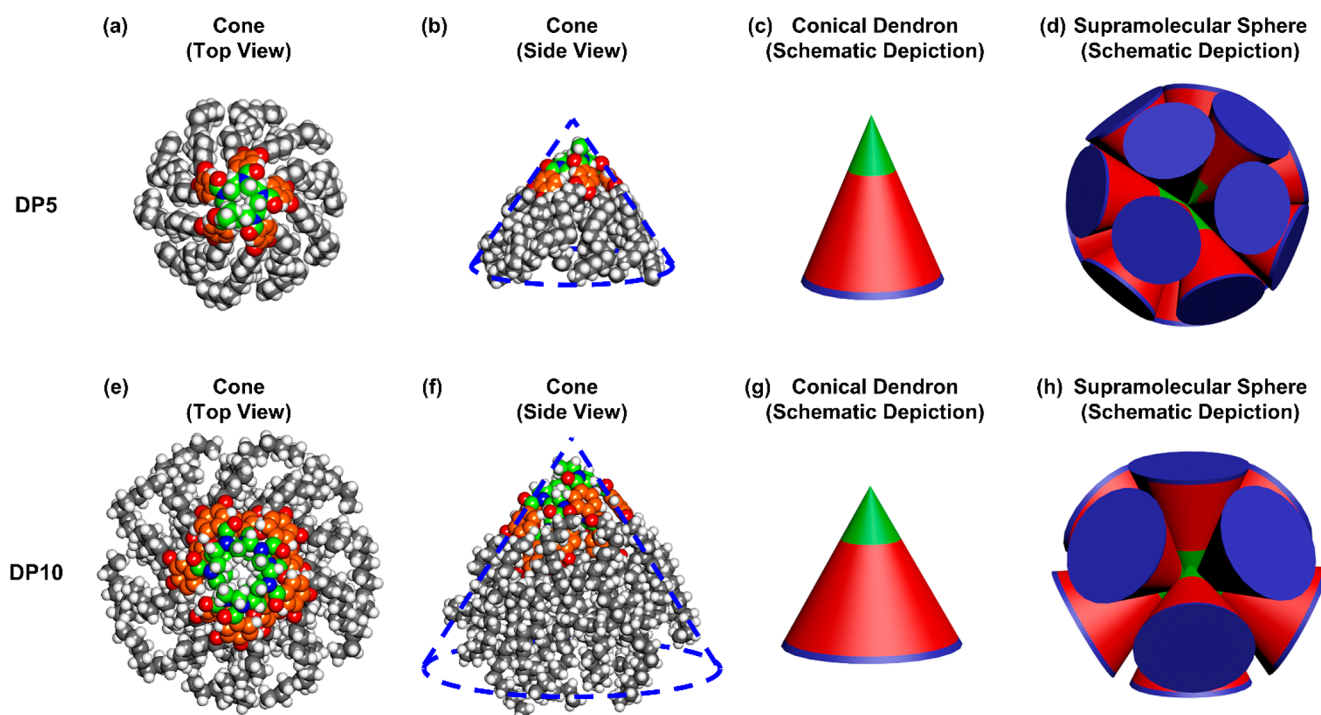


Figure 3. Molecular models of supramolecular spheres of (a–d) DP5 and (e–h) DP10. Conical dendron viewed along (a, e) long axis and (b, f) side. (c, g) Schematic depiction of conical dendron. (d, h) Supramolecular spheres constructed from (d) 16 conical dendrons and (h) 10 conical dendrons. Color code used in the molecular models (a, b, e, and f): O atoms, red; H atoms, white; N atoms, blue; C atoms in the core, green; C atoms in the phenyl rings, orange; C atoms in the alkyl chains, grey.

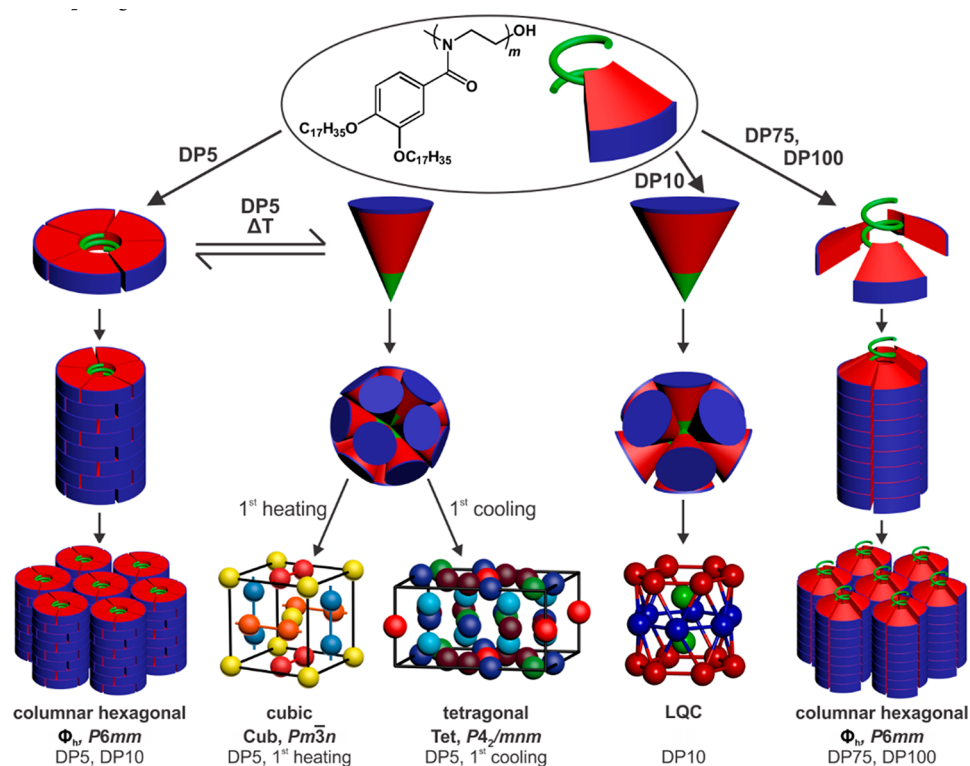


Figure 4. Summary of periodic and quasicrystalline arrays self-organized from assemblies of poly[(3,4)17G1-Oxz].

as a driving force for the different self-organization behavior of DP5 and DP10 is not immediately obvious and requires further study.

Poly[(3,4)17G1-Oxz] self-organizes into a dodecagonal liquid quasicrystal unprecedented for poly(2-oxazoline)s. In

addition, by varying the degree of polymerization between only DP5 and DP10, two periodic approximants to the LQC, the $Pm\bar{3}n$ Cub or $P4_2/mnm$ Tet phases, were self-organized from this single dendronized polymer (Figure 4). Retrostructural analysis suggests that similar spherical assemblies are generated

by DP5 and DP10. Furthermore, an almost identical polymer, poly[(3,4)16G1-Oxz],²⁴ did not self-organize into the LQC phase. The observation of all three of these arrays from a single polymer chain in only five monomer repeat units (DP5 and DP10) raises fundamental questions with respect to the relative stability of these Frank–Kasper phases and the driving forces for their formation. Encouragingly, the polymer reported here may facilitate development of theoretical frameworks to investigate self-organization of complex soft matter into Frank–Kasper phases, due to the structural diversity exhibited during its self-organization. Hence the results herein are expected to stimulate both experimental and theoretical investigations into the formation of multiple periodic and quasiperiodic arrays from single molecular entities based on dendronized polymers, supramolecular polymers, and other complex soft matter. It is remarkable that only 52 years after the discovery of the living cationic ring-opening polymerization of 2-oxazolines,²⁹ some of the most complex supramolecular architectures discovered in soft condensed matter (Figure 4) can be so easily accomplished with this methodology. The discovery of Frank–Kasper phases across synthetic and biological soft condensed matter and solution states^{2–24} together with recent progress on the polymerization of cyclic imino ethers^{22,24} provides an enthusiastic driving force for interdisciplinary studies in this area.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b11103.

Synthetic procedures with complete characterization data, and experimental methods (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*percec@sas.upenn.edu

ORCID

Benjamin E. Partridge: 0000-0003-2359-1280

Mihai Peterca: 0000-0002-7247-4008

Goran Ungar: 0000-0002-9743-2656

Virgil Percec: 0000-0001-5926-0489

Present Address

[†]D.S.: Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, United States.

Notes

The authors declare no competing financial interest.

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